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DETAILED DESCRIPTION

[Detailed description]

[0001]

[The technical field to which invention belongs] It decomposes in a natural environment and this invention relates to the biodegradability laminated film excellent in heat-sealing nature and transparency.

[0002]

[A Prior art and Object of the Invention] The general packing-material intended use which made the snack confectionery bag the typical example is begun, and the plastics film which was excellent in broad intended use, such as agricultural materials, construction materials, and a medical material, at transparency and heat-sealing nature is demanded

[0003] Transparency is usually expressed by the light transmission. Since what has high permeability is excellent in transparency and a contents can see it from an outside, it is used by preference as a wrapping.

[0004] In case the so-called "heat sealing" of the film excellent in heat-sealing nature which sticks a film comrade by heat and the pressure, or is pasted up using a heating bar, a hot plate or a heating roller, etc. is carried out, it points to the film with the wide temperature requirement obtained by being stabilized in the bond strength for which it asks. That is, the film excellent in heat-sealing nature can obtain various kinds of film manipulation products simple by heat sealing.

[0005] On the other hand, it is asked for the plastics product which does not affect the natural environment which decomposes and disappears with time when it is rejected from the rise about an environmental problem in a natural environment to a plastic-working article at large in recent years.

[0006] However, the trouble of the conventional plastics film product being stable over the long period of time in the natural environment, and a buld specific gravity having promoted short-lived-ization of an eccrisis reclaimed ground moreover for a parvus reason, or spoiling a natural scene and the living environment of wild nature animals and plants was pointed out.

[0007] Then, the biodegradable plastic material attracts attention today. Biodegradable plastics are the inside of soil, and underwater, according to hydrolysis or biodegradation, a decay and decomposition advance gradually and becoming a harmless decomposition product by operation of a microorganism finally is known.

[0008] Now, the biodegradable plastic by which utilization is considered is divided roughly into aliphatic polyester and denaturation PVA (polyvinyl alcohol), a cellulose-ester compound, the starch denaturation field, and these blends field.

[0009] However, in the biodegradable plastic mentioned above, heat-sealing nature and transparency equivalent to the polyethylene used conventionally, polypropylene, a polyethylene terephthalate, etc. cannot be acquired.

[0010] Then, the purpose of this invention is to offer the biodegradability laminated film excellent in heat-sealing nature and transparency, having a biodegradability.

[0011]

[The means for solving a technical problem] It is the biodegradability laminated film characterized by preparing the unstretched film containing different biodegradability aliphatic [a polylactic-acid system polymer and a polylactic-acid system polymer]-to one [at least] oriented-film side which consists of constituent with which summary of this invention makes principal component polylactic-acid system polymer or this polyester. The melting point of the aforementioned oriented film has the desirable biodegradability laminated film of the claim 1 publication characterized by being higher than the melting point of the aforementioned unstretched film. The summary of a different this invention is a biodegradability laminated film characterized by preparing the unstretched film containing different biodegradability aliphatic [a polylactic-acid system polymer and a polylactic-acid system polymer]-to one [at least] biodegradability cellulose film side polyester.

[0012]

[Gestalt of implementation of invention] The polylactic-acid system polymers used for this invention are the copolymers of a polylactic acid or a lactic acid, and other hydroxycarboxylic acid, or these constituents, and can mix other polymeric materials in the domain which does not check the effect of this invention. Moreover, it is also possible to add additives, such as a plasticizer, a lubricant, an inorganic filler, and an ultraviolet ray absorbent, and a modifier in order to adjust the physical properties and workability of a film.

[0013] As a lactic acid, L-lactic acid and D-lactic acid are mentioned and a glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, a 3-hydroxy valeric acid, a 4-hydroxy valeric acid, a 6-hydroxy caproic acid, etc. are typically mentioned as hydroxycarboxylic acid.

[0014] The polymerization method is possible also for adopting well-known technique, such as condensation-polymerization nature and a ring-opening-polymerization method, and may use a little chain extension agent, for example, a diisocyanate compound, a diepoxy compound, an acid anhydride, acid chloride, etc. for the purpose of molecular weight increase further. The problem of the domain of 60,000 to 1000 and 000 being desirable, and lower ***** and practical use physical properties hardly being discovered in such a domain as weight average molecular weight of a polymer, is produced. Moreover, a melt viscosity becomes high too much and is inferior to an upper ***** case at fabricating-operation nature.

[0015] For extending a polylactic-acid system film, a flat drawing machine, a tubular formula drawing machine, etc. of a roll formula or a tenter formula are used. Extension temperature chooses a draw magnification from the glass transition temperature of a polylactic-acid system polymer within the limits of crystallization temperature, taking into consideration the amount of preferred orientation of a film by 6 or less-time within the limits to at least 1 shaft orientations. The polylactic-acid system film which has crystallinity is used and a film is heat-treated several seconds or more by within the limits from the crystallization temperature of the film after extension to the melting point to stop a thermal contraction.

[0016] It is desirable that the melting point T_m of an oriented film which consists of a constituent which makes a principal component a polylactic-acid system polymer or this is 100 degrees C or more. At less than 100 degrees C, thermal resistance falls and T_m tends to cause a wrinkling etc. in a fabricating etc. Moreover, T_m of a poly-L-lactic acid gay polymer is 195 degrees C, and T_m falls as copolymerization components, such as D-lactic acid, a glycolic acid, and a 6-hydroxy caproic acid, increase. For this reason, in practice, T_m s of the oriented film mentioned above are 100 degrees C or more and 195 degrees C or less.

[0017] The unstretched film used by this invention contains the biodegradability aliphatic polyester different from a polylactic-acid system polymer and a polylactic-acid system polymer. A polylactic-acid system polymer can use the same polylactic-acid system polymer as what was mentioned above.

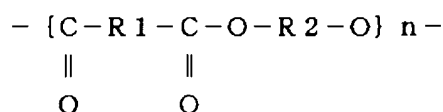
[0018] On the other hand, different aliphatic polyester does not have an alkylene and ester combination as basic skeleton, is the domain which does not have real influence on a biodegradability, and, as for a polylactic acid, can also introduce a urethane bond, amide combination, ether linkage, etc. Especially, using an isocyanate compound, a urethane bond can be introduced into a principal chain and molecular weight can be jumped up.

[0019] The compound shown in the generalization 1 specifically obtained by condensing in an aliphatic

diol and an aliphatic dicarboxylic acid is mentioned.

[0020]

[-izing 1]



(The inside R1 and R2 of a formula is the alkylene machine, the cyclo ring machine, or cyclo alkylene machine of carbon numbers 2-10.) Moreover, n is polymerization degree required to become number average molecular weight 10,000-150,000. Amide combination, a urethane bond, carbonate combination, or alpha-hydroxycarboxylic acid may be contained in addition to this basic structure. As an aliphatic diol, ethylene glycol, 1, 4-butanediol and 1, and 4-cyclohexane dimethanol etc. is mentioned, and a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are typically raised as an aliphatic dicarboxylic acid. After choosing one or more kinds from these, respectively and carrying out a condensation polymerization, the polymer which jumped up weight average molecular weight or more to 50,000 with the isocyanate compound if needed can have the usually same basic physical properties as 60-110-degree C Tm and polyethylene, and can use them for this invention preferably.

[0021] Moreover, a series of aliphatic polyester which carried out the ring opening polymerization of the annular lactone using the organic-metal catalyst is mentioned. As a monomer, epsilon-caprolactone, delta-valerolactone, a beta-methyl-delta-valerolactone, a beta propiolactone, ***** lactone, beta-butyrolactone, gamma-butyrolactone, etc. are mentioned typically, and a lactide and glycolide are mentioned further. Conditions are adjusted and a polymerization is carried out so that one or more kinds may be chosen out of these and weight average molecular weight may become 30,000 or more.

Although a control of Tm is performed by selection of a monomer, it is usually 50-170 degrees C.

[0022] As other synthetic system aliphatic polyester, the radical polymerization field with the 2-methylene -1 which are a cyclic anhydride, oxy-runs, for example, a succinic anhydride and an ethyleneoxide, a propione oxide or the polymer of allyl glycidyl ether, and ethylene and an annular ketene acetal, 3-dioxolane and the 2-methylene -1, and 3-dioxepane etc. is mentioned.

[0023] Moreover, the aliphatic polyester biosynthesized by acetyl-coenzyme A (acetyl CoA) within the biomass including the *Alcaligenes* ***** is known. Although it is mainly Polly beta-hydroxybutyric acid (poly 3HB), in order to put the practical use property as plastics on **, as for this aliphatic polyester, it is industrially advantageous to devise a fermentation process, to usually carry out copolymerization of the valeric-acid unit (HV), and to make it the copolymer of poly (3HB-co-3HV). Generally HV copolymerization ratio is 0 - 40%, and Tm is 130-165 degrees C in this domain. Copolymerization of the 4HB may be carried out instead of HV, or copolymerization of the hydroxy alkanoate of a long chain may be carried out.

[0024] Although polyvinyl alcohol (PVA) is comparatively excellent in the biodegradability in the existing petroleum origin synthesis system polymer, PVA homopolymer has the too large cohesive force of a molecule, and since melting extrusion molding is not made without the melting point, when film-izing, the constraint on a fabricating operation is received. Then, copolymerization of the ethylene can be carried out or the vinyl acetate unit which usually disappears at a saponification process can be made to be able to remain, and it can reform and use so that it may have Tm of 50-150 degree-C grade. In order to raise a biodegradability for such a PVA system polymer to the base, the constituent which distributed starch etc. is the so-called denaturation PVA, and can use it for this invention.

[0025] The film which consists of a cellulose or its derivative, for example, the acetyl cellulose acetylated to the grade holding cellophane or a biodegradability, is raised, and the biodegradability cellulose film used by this invention can be obtained by the solvent cast formula or the melting extrusion formula.

[0026] The unstretched film containing the biodegradability aliphatic polyester different from a

polylactic-acid system polymer and a polylactic-acid system polymer is produced as follows. There is the technique of extruding in the technique of extruding both from a mouthpiece, after feeding a raw material into the same extruder, respectively, and producing a direct film, or a strand configuration, producing a pellet, and producing a film with an extruder again. It is better to choose the latter for making it mix uniformly, although all must take into consideration a fall of the molecular weight by decomposition. After fully drying the aliphatic polyester different from a polylactic-acid system polymer and a polylactic-acid system polymer and removing moisture, melting is carried out with an extruder. A polylactic acid chooses a melting extrusion temperature suitably by the composition ratio of L-lactic acid structure and D-lactic-acid structure in consideration of the rate of the thing which the melting point changes, and mixture of both. An about 100-250-degree C temperature requirement is usually chosen.

[0027] As for the rate of mixture of the aliphatic polyester different from a polylactic-acid system polymer and a polylactic-acid system polymer, it is desirable to make it the domain of 75:25-20:80 by the polymerization ratio. If the rate of a polylactic-acid system polymer exceeds 75%, the film obtained will become a crack, *****, and the thing that becomes empty and that is hard to treat practically for the hardness originating in a polylactic acid, and brittleness. On the other hand, transparency is inferior when the rate of a polylactic-acid system polymer is less than 20%. Usually, if a light transmission is 75% or more preferably 65% or more, a transparent feeling will serve as a high film.

[0028] In the biodegradability laminated film of this invention, the oriented film which consists of a constituent which makes a principal component a polylactic-acid system polymer or this serves as supporters, and the unstretched film containing the biodegradability aliphatic polyester different from a polylactic-acid system polymer and a polylactic-acid system polymer serves as a heat-sealing layer.

[0029] As for the melting point of the supporters who are the oriented films mentioned above, it is desirable that it is higher than the melting point of the heat-sealing layer which is the unstretched film mentioned above. By making the melting point high, supporters do melting at the time of seal work, Siwa etc. does not occur, and a setup of seal conditions becomes easy. It is that the melting point of an oriented film is higher than the melting point of a unstretched film 10 degrees C or more still preferably.

[0030] The oriented film which serves as supporters has the melting point. Since the amorphous film which does not have the melting point cannot do a heat setting, heat-resistant temperature will become below a glass transition point. With the amorphous film of a polylactic-acid system polymer, heat-resistant temperature becomes 60 degrees C or less, and cannot use it as supporters.

[0031] In the biodegradability laminated film of this invention, a biodegradability cellulose film can be used as supporters. As mentioned above, cellophane, an acetyl-cellulose film, etc. are mentioned to a biodegradability cellulose film. The so-called heat-resistant temperature from which a light transmission is 90% or more, and appearance change of a foaming etc. produces these biodegradability cellulose films is 160 degrees C or more.

[0032] In order to obtain the laminated film of this invention, there are the technique of sticking a film with adhesives, technique of carrying out thermocompression bonding of the two films in an optimal temperature with a hot platen or a roll, technique that while started winding, and extrudes and coats a film with the material which constitutes the film of another side.

[0033] Also of the technique mentioned above, the dry lamination or the wet lamination method for using adhesives is simple. As adhesives, a vinyl system, acrylic, the polyamide system, the polyester system, the rubber system, the urethane system, etc. are common. Furthermore, when also making adhesives into a biodegradability, protein, such as polysaccharide, such as starch, an amylose, and an amylopectin, and the glia, gelatin, casein, a zein, a collagen, polypeptides, non-cured natural rubber, or the urethane that makes aliphatic polyester and aliphatic polyester a principal component is desirable.

[0034]

[Example] Hereafter, although an example is explained, this invention is not limited to this.

[0035] The monolayer which might be mentioned later or the light transmission of a laminated film, and heat-sealing nature were measured as follows.

[0036] (1) Light-transmission JIS It measured based on K7105. Excelling in transparency is shown so that a value is large.

[0037] (2) In the case of the simple substance film, in the case of the two-layer film, as it was, two sheets were arranged, the film test piece which cut down the heat-sealing nature film in 100mm and the size of 15mm of the cross direction at the longitudinal direction was piled up so that sealing layers might face, and one end was heat sealed to 10mm width of face at right angles to a longitudinal direction. A sealing surface is set to 15mmx10mm. Using the metal heating bar with a width of face [in which a temperature control is possible on a seal] of 10mm, it presupposed that it is fixed with pressure 1.0kgf/cm², and seal time 3 seconds, the temperature of a heating bar was changed, and seal nature was evaluated. In addition, in order to suppress the weld with the heating bar of a film as much as possible, the tape which consists of the ground made from Teflon is stuck on the heat transfer side of a heating bar. Evaluation investigated appearance change and the intensity of a seal fraction.

[0038] The intensity extended each sample and asked for the maximum intensity which the part which carried out [the part] the chuck to the tension tester and carried out the seal to it exfoliates or fractures. The intensity per width of face of 15mm (kgf / 15mm) showed the seal intensity. The tension test was performed by 80mm, 100mm of speed of testings, and min between chucks using Oriental energy machine Tensilon 2 Type Machine.

[0039] Lacty (Shimadzu Make) which consists of a [example 1 of experiment] polylactic acid was extruded from the T die at 220 degrees C by 60mmphi single screw extruder, it quenched with a casting roll, and the non-extended sheet with a thickness of about 140 micrometers was obtained.

[0040] This non-extended sheet was continued, it roll-extended 2.3 times at 75 degrees C, and ranked second to a longitudinal direction at them, at them, and it extended by the tenter crosswise and extended 2.5 times at 70 degrees C. Then, it heat-treated in temperature of 120 degrees C, and processing-time 25 seconds in the heat treatment zone of a tenter, and the 20-micrometer biaxial-orientation extension polylactic-acid film was obtained.

[0041] Moreover, after carrying out mixed melting of the Bionolle #1001 (Showa High Polymer Co., Ltd. make) which consists of a condensation product of Lacty (Shimadzu Make), 1 and 4-butanediol, and the succinic acid which consist of a polylactic acid at a rate of 70:30 using the 25mmphi said orientation small biaxial extruder, it extruded in the strand configuration at about 200 degrees C, and the pellet was produced. Next, the unstretched film of 40 micrometer ** was produced at the casting humidity of 52 degrees C using the 30mmphi small single screw extruder.

[0042] Two kinds of obtained films were stuck. It stuck, and one side of both films was pasted up on doubling by the dry lamination formula, after performing corona surface treatment for energy 24W/m²/beforehand. That is, the polyurethane system solvent type adhesive was uniformly applied to the processing side of a polylactic-acid biaxial oriented film so that it might be about set to 1 micrometer, another film was piled up so that a processing side might suit adhesives, and it was stuck by pressure with the roller. To it, it let it pass during several seconds to the drying furnace continuously set up at 70 degrees C, dried, and aged for three days at 40 more degrees C.

[0043] As biodegradability aliphatic polyester other than the polylactic acid used for the [example 2 of experiment] unstretched film, the biodegradability laminated film was obtained like the example 1 of an experiment except having used 1 and Bionolle #3001 (Showa High Polymer Co., Ltd. make) which are ***** coalesce of 4-butanediol, and a succinic acid/adipic acid.

[0044] The biodegradability laminated film was obtained like the example 2 of an experiment except having set to 70:30 to 50:50 and 25:75 the composition ratio of the polylactic-acid system polymer used for the [examples 3 and 4 of experiment] unstretched film, and biodegradability aliphatic polyester other than a polylactic acid.

[0045] As biodegradability aliphatic polyester other than the polylactic acid used for the [example 5 of experiment] unstretched film, the biodegradability laminated film was obtained like the example 3 of an experiment except having used the plaque cell H7 (Daicel Chemical Industries, Ltd. make) which consists of a poly-caprolactone.

[0046] it took over, quenching by ***** made into 57 degrees C of skin temperatures, after carrying out melting push appearance of Lacty (Shimadzu Make) which consists of a [example 6 of experiment] polylactic acid using a 30mmphi small single screw extruder, and the film with a thickness

of 40 micrometers was produced

[0047] [Example 7 of an experiment] 1 and Bionolle #1001 (Showa High Polymer Co., Ltd. make) which consist of a condensation product of 4-butanediol and a succinic acid obtained the monolayer film of 40 micrometer ** at the casting temperature of 52 degrees C using 30mmphi and the small single screw extruder.

[0048] The unstretched film obtained in the example 3 of the [example 8 of experiment] experiment was used as it was.

[0049] The film obtained in the oriented film in the example 1 of the [example 9 of experiment] experiment and the example 7 of an experiment was stuck by the same technique as the example 1 of an experiment.

[0050] Transparent cellophane with a [example 10 of experiment] thickness of 21 micrometers and the unstretched film [finishing / corona surface treatment] obtained in the example 2 of an experiment were stuck by the same technique as the example 1 of an experiment.

[0051] Transparent cellophane with a [example 11 of experiment] thickness of 21 micrometers and the unstretched film which carried out corona surface treatment of the film obtained in the example 7 of an experiment were stuck by the same technique as the example 1 of an experiment.

[0052] A light transmission and heat-sealing nature were investigated about the sample obtained in the examples 1-11 of an experiment mentioned above. the result of the examples 1-5 of an experiment -- Table 1 -- said -- the result of 6-9 -- Table 2 -- said -- the result to 10-11 is shown in Table 3 In addition, comprehensive evaluation was shown in four phases of OO**x. O -** -- a practical use domain -- it is -- x -- practical use -- a thing out of range is shown For the sample of the examples 1-5 of an experiment, the example of this invention and the examples 6-9 of an experiment are [the example of this invention and the example 11 of an experiment of the example of a comparison and the example 10 of an experiment] examples of a comparison.

[0053]

[Table 1]

表 1

実験番号		1	2	3	4	5
延伸フィルム	ポリ乳酸系重合体	ラテ1012	ラテ1012	ラテ1012	ラテ1012	ラテ1012
	融点 (°C)	175	175	175	175	175
	厚み (μm)	20	20	20	20	20
未延伸フィルム	ポリ乳酸系重合体 (重量%)	ラテ1012 (70)	ラテ1012 (70)	ラテ1012 (150)	ラテ1012 (25)	ラテ1012 (25)
	ポリ乳酸以外の生分解性脂肪族ポリエステル (重量%)	バイオレ1001 (30)	バイオレ3001 (30)	バイオレ3001 (50)	バイオレ3001 (75)	ラテカH7 (50)
	融点 (°C)	114	96	96	96	60
	厚み (μm)	40	40	40	40	40
光線透過率 (%)		75	93	91	78	68
ヒートシール性 (kgf/15mm)	80 (°C)	0.1以下	シールできない	0.1以下	シールできない	0.3
	100	0.1以下	1.4	1.6	1.7	1.3
	120	1.6	1.8	2.0	2.1	1.4
	140	2.0	2.2	2.4	2.5	1.4
	160	変形	変形	変形	変形	変形
総合評価		○	◎	◎	○	△
本発明か否か		本発明	本発明	本発明	本発明	本発明

[Table 2]

表 2

実験番号		6	7	8	9
延伸フィルム	ポリ乳酸系重合体	—	—	—	ラテ1012
	融点 (°C)	—	—	—	175
	厚み (μm)	—	—	—	20
未延伸フィルム	ポリ乳酸系重合体 (重量%)	ラテ1012 (100)	—	ラテ1012 (50)	—
	ポリ乳酸以外の生分解性脂肪族ポリエステル (重量%)	—	ビオノール1001 (100)	ビオノール3001 (50)	ビオノール1001 (100)
	融点 (°C)	175	114	96	114
	厚み (μm)	40	40	40	40
光線透過率 (%)		99	59	90	58
ヒートシール性 80 (°C) (kgf/15mm)		シールできない シールできない シールできない シールできない シールできない	シールできない 0.1以下 1.1 2.2 2.2	シールできない 0.1以下 0.3 1.0 変形	シールできない 0.1以下 1.4 2.6 変形
総合評価		×	×	×	×
本発明か否か		否	否	否	否

[Table 3]

表 3

実験番号		10	11
生分解性セルロースフィルムとその厚み (μm)		セロファン (20)	セロファン (20)
未延伸フィルム	ポリ乳酸系重合体 (重量%)	ラテ1012 (50)	—
	ポリ乳酸以外の生分解性脂肪族ポリエステル (重量%)	ビオノール3001 (50)	ビオノール1001 (100)
	厚み (μm)	40	40
光線透過率 (%)		90	57
ヒートシール性 80 (°C) (kgf/15mm)		0.2 1.2 2.2 2.6 2.7 (ヒートシール)	0.2 1.3 2.1 2.3 2.2 (ヒートシール)
総合評価		◎	×
本発明か否か		本発明	否

As for both the laminated films of this invention which consists of a unstretched film containing the oriented film which consists of a constituent which makes a principal component a polylactic-acid system polymer or this, and the biodegradation aliphatic polyester different from a polylactic-acid system polymer and a polylactic-acid system polymer, a light transmission and heat-sealing nature are settled in practical use within the limits so that clearly from Table 1. On the other hand, in the example of a comparison shown in Table 2, a light transmission or heat-sealing nature has deteriorated.

Moreover, as shown in Table 3, even if it uses a biodegradability cellulose film for supporters, it excels in the laminated film of the configuration of this invention at a light transmission and heat-sealing nature.

[0054]

[Effect of the invention] As mentioned above, as explained, since the laminated film of this invention has the transparency and heat-sealing nature which were excellent, using the material which has a biodegradability, it is suitable for the manufacture of an eco-friendly **** material etc.

[Translation done.]